DFT Calculations of Magnetic Resonance Parameters for Heavy-Element Compounds

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The accurate calculation of NMR and EPR parameters for compounds containing transition metals and/or heavy main-group atoms requires the simultaneous inclusion of electron correlation and of the dominant relativistic effects.[1] We report on our progress in calculating magnetic resonance parameters, using DFT approaches and including relativistic effects. Spin-orbit effects may be included by perturbation theory. This is done either in an all-electron fashion (using explicit Breit-Pauli or Douglas-Kroll two-electron spin-orbit integrals or a recently implemented one-center/meanfield approximation[2] to these integrals) or with spin-orbit pseudopotentials (together with scalar relativistic pseudopotentials at the Kohn-Sham stage of the calculations). Pseudopotential and meanfield/all-electron spin-orbit operators may even be used in a combined fashion. Application examples will cover, e.g., spin-orbit effects on NMR chemical shifts, and EPR electronic g-tensors. The latter are of particular interest by being an intrinsically „relativistic" property. A new relativistic all-electron DFT approach is being implemented, based on the Douglas-Kroll transformation. The aim is a) to calculate relativistically magnetic resonance parameters involving the heavy centers themselves and b) to include spin-orbit coupling explicitly in a two-component scheme. First results obtained with this new code will be discussed.

[1] Reviews: M. Kaupp, V. G. Malkin, O. L. Malkina, in P. v. R. Schleyer (Ed.), *Encyclopedia of Computational Chemistry*; Wiley: New York, 1998; pp. 1857ff. M. Bühl, M. Kaupp, O. L. Malkina, V. G. Malkin *J. Comp. Chem.* **1999**, *20*, 91.[2] O. L. Malkina, B. Schimmelpfennig, M. Kaupp, B. A. Hess, P. Chandra, U. Wahlgren, V. G. Malkin *Chem. Phys. Lett.* **1998**, *296*, 93.